III.B.5 Fundamental Reforming Studies - Role of Catalytic O_2 Supports on Fuel Reforming

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Objectives

- Investigate the role of oxygen-conducting supports in hydrocarbon reforming and their role in decreasing carbon formation and/or increasing sulfur tolerance.
- Develop a fundamental knowledge base for developing more long-duration reforming catalysts for auxiliary power units.

Approach

- Carbon formation, catalytic activity, H_2 selectivity, and catalyst stability are the main catalytic parameters studied during the partial oxidation reaction of CH_4 and higher hydrocarbons.
- Several sample matrices of ceria-based catalysts are studied to elucidate the effect of the following catalyst variables in the partial oxidation of methane and higher hydrocarbons:
  - metal type (Pt, Ni, Rh)
  - support type (CeO_2 and Al_2O_3)
  - catalyst ionic conductivity
  - dopant type (La, Gd, Zr)
  - dopant concentration (GDC10 & GDC30)
  - oxygen storage capacity
- Catalyst characterization includes ionic conductivity, surface area, crystal phase and catalyst reduction temperature.
- Experimental variables include temperature, space velocity, oxygen/carbon ratio and time on stream.
- Mechanistic studies include
  - Labeling doped ceria catalysts with $^{18}O_2$,
  - Conducting the partial oxidation of methane (POM) reaction over $^{18}O_2$ labeled catalysts, and
  - Performing prior and post reaction experiments by Nuclear Reaction Analysis (NRA) to complement the isotopic studies and obtain ^{18}O concentration profiles and total oxygen concentration in the catalysts.
- Studies related to sulfur tolerance are planned for the following stage of this project.
- Partial oxidation of higher hydrocarbons than CH_4 is planned for the following stage of this project.

Accomplishments

- Catalyst characterization has been completed, which included ionic conductivity, surface area, crystal phase and catalyst reduction temperature.
- Several sample matrices of ceria-based catalysts which include materials with different metal type, support type, dopant type and dopant concentration have been tested during the partial oxidation of methane, having as experimental variables temperature, space velocity, oxygen/carbon ratio, and time on stream.
- This work has revealed that catalysts with higher ionic conductivity show a trend towards less carbon formation than in materials with lower ionic conductivity.
- Doped Pt-based catalysts showed higher stability in CH_4 conversion than doped Rh (although similar) and Ni based catalysts.
- Pt/CeO_2 showed higher and more stable CH_4 conversion than Pt/Al_2O_3, mainly due to the higher oxygen storage capacity of the former catalyst.
- Mechanistic studies have been initiated by labeling doped ceria catalysts with $^{18}O_2$.
- A review paper was published.
- A Solid State Energy Conversion Alliance (SECA) merit review was conducted.
- An oral presentation has been accepted to be presented at the American Institute of Chemical Engineers (AIChE) Fall Meeting, 2005.

Future Directions

- Conduct the POM reaction over $^{18}O_2$ labeled catalysts.
- Collaborate with Pacific Northwest National Laboratory to determine ^{18}O concentration profiles and total oxygen concentration in the catalysts by NRA analysis prior and post reaction experiments.
- Determine/correlate NRA results with amount of carbon generated during catalytic studies.
- Determine lattice oxygen contribution in products generation during partial oxidation reactions.
- Determine catalytic activity of doped ceria catalysts in the absence of gaseous oxygen to correlate results with oxygen storage capacity.
- Studies related to sulfur tolerance will be conducted.
- Partial oxidation of higher hydrocarbons will be conducted.

Introduction

The U.S. Department of Energy is sponsoring development of high-temperature fuel cell power systems based on solid oxide technology through its Solid State Energy Conversion Alliance (SECA) program. The program is geared toward mass manufacturing of fuel cells for high-volume markets and multiple applications. One of those markets/ applications is a diesel-fueled auxiliary power unit (APU) for long-haul truck transportation. The fuel processor is a critical component of this system and must be able to provide a clean, tailored synthesis gas to the fuel cell stack for long-term operation. Key characteristics desired for the processor (and the system) include low cost, high efficiency, maximum thermal integration, low maintenance intervals, and acceptable startup and transient response. There are also several barrier issues that must be overcome to achieve these characteristics. Carbon formation, particularly upon startup, must be minimized to avoid coking of the catalysts in the reformer and downstream fuel cell. Fuels containing sulfur can poison both the reforming catalysts and the fuel cell anode.

Ceria-based catalysts are being investigated in this work in order to fundamentally understand the role of oxygen-conducting supports in reforming of diesel fuel compounds and their role in decreasing carbon deposition. Ceria-based catalysts have shown ability to decrease carbon formation during partial

oxidation of hydrocarbons [1,2]. It has been speculated that this property is due to the high oxygen ion mobility of the catalysts. In this project, this assumption is investigated, and an attempt is made to obtain a reaction mechanistic scheme to get a better understanding of carbon formation and mitigation.

Approach

Carbon formation, catalytic activity, H_2 selectivity, catalyst reducibility and stability were studied during the partial oxidation of methane (POM). Catalyst variables included metal type (Pt, Ni, Rh), support type (Al_2O_3 and CeO_2), catalyst ionic conductivity, dopant type (La, Gd, Zr), dopant concentration (GDC10 & GDC30) and oxygen storage capacity. More than a hundred experiments were carried out to study the influence of the following variables: temperature, oxygen/carbon ratio, time on stream and space velocity. Characterization of ceria-based catalysts included catalyst phases, ionic conductivity, temperature-programmed reduction profiles and surface areas. A tubular reactor was used to conduct the experimental tests during the POM reaction. A ceramic furnace heated the reactor, and a thermocouple was centered within the catalyst bed to measure and control the reaction temperature. Typically, a 250-mg sample was placed in the middle of the reactor, using sand as the packing material. The reaction was conducted at 700ºC. In general, mixtures of 10% CH_4, 5% O_2 (oxygen/carbon ratio O/C=1), balance N_2 at a total flow rate of 324 cm^3/min (standard temperature and pressure) were delivered to the reactor. The reacting gases were all certified with helium (99.999%), used without any further purification. A mass spectrometer connected on line analyzed the feed and product gas streams. A cold trap at the outlet of the reactor was used to condense out any water from the product gas stream. Preliminary studies to screen the catalytic activity of pure CeO_2 and sand at 700°C were conducted prior to the catalyst testing. Low conversions of methane on sand and pure ceria were detected: 15% and 20%, respectively. Carbon monoxide and H_2 were not detected; CO_2 was the only product.

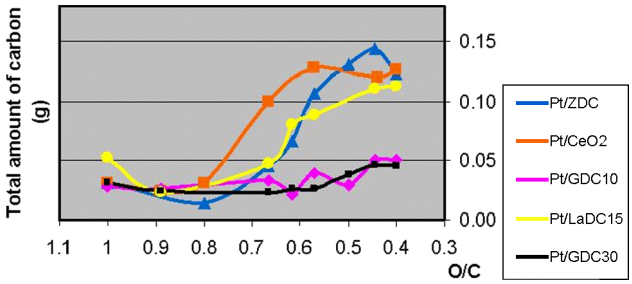

Figure 1. Carbon Formation vs. O/C on Pt Catalysts during the POM Reaction at 700°C

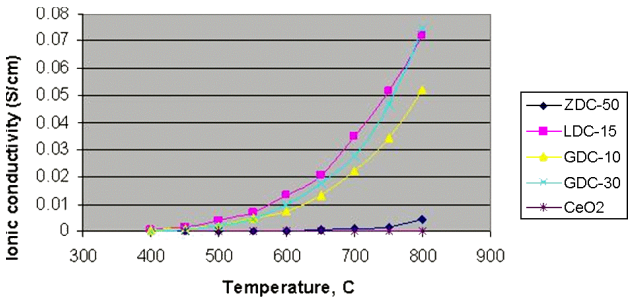

Figure 2. Ionic Conductivity of Doped Ceria Supports

Results

During the second year of the project, significant progress was demonstrated on all main tasks. Only the main results are presented here. In order to study the influence of ionic conductivity on carbon formation, carbon formation was observed during partial oxidation of methane (POM) using ceria-doped catalysts. Results showed a correlation between the ionic conductivity of the catalysts and the amount of carbon generated. Catalysts with higher ionic conductivity showed a trend towards less carbon formation than in the materials with lower conductivity (Figure 1). A lower amount of carbon was obtained by Pt/GDC10 and Pt/GDC30. The ability of these catalysts to mitigate carbon formation may be due to the high oxygen ion mobility (ionic conductivity) of the doped ceria supports that speeds the surface carbon oxidation and avoids the catalyst deactivation. The higher ionic conductivity shown by GDC15, GDC30 and GDC10 compared to ZDC and the un-doped CeO_2 (Figure 2) may be correlated to the close ionic radii of Gd^{3+} and La^{3+} cations compared to that of the Ce^{4+} cation. When there is a mismatch between the dopant and the host radii, a minimum in the binding energy between ion vacancies and dopant cations is

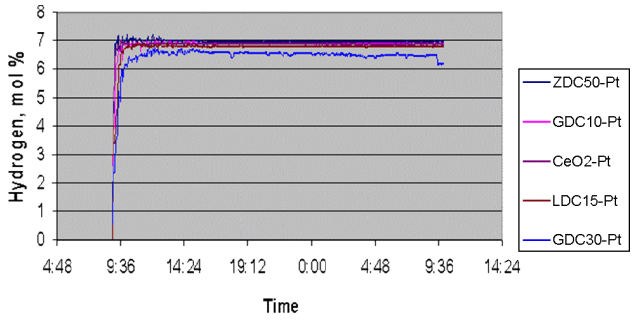

Figure 3. Stability of Pt Catalysts during the POM Reaction at O/C=0.4 and 700°C

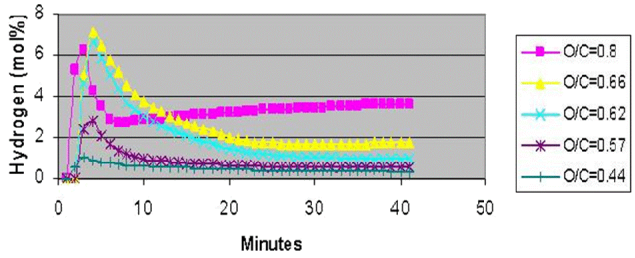

Figure 4. H_2 Generation vs. O/C Ratio during the POM Reaction on Pt/Alumina at 700°C

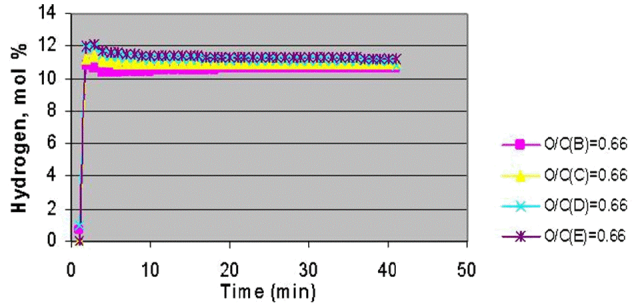

Figure 5. Regeneration of Catalytic Activity of Pt/GDC10 during POM Reaction at 700°C

predicted, resulting in high values of ionic conductivity [3]. Pt-ceria doped catalysts were highly active and selective for the POM reaction and showed stable performance for at least 20 h. This reaction was carried out at lower oxygen concentration (oxygen/carbon ratio=0.4) than the stoichiometric required to accelerate deactivation due to carbon formation. Results showed that all catalysts maintained stable conversion through the whole testing period (Figure 3). The POM reaction was also carried out on Pt/Al_2O_3 in the oxygen/carbon ratio range of 0.8 to 0.4 (Figure 4). Results showed deactivation and loss of catalytic activity in a short period of time, which may be due to the lower oxygen storage capacity this material has compared with Pt-ceria based catalysts. After conducting the POM reaction on Pt-ceria based catalysts, the generated carbon was oxidized with air and the reaction was immediately re-run on the same catalysts without any further catalyst pretreatment. Results showed that catalysts were fully regenerated after carbon build-up, and initial conversions and selectivity were recovered (Figure 5).

Conclusions

- We found a general correlation between the ionic conductivity of doped ceria catalysts and the amount of carbon generated. Catalysts with higher ionic conductivity showed a trend towards less carbon formation than in the materials with lower conductivity. The decreasing order trend in carbon formation is: Pt/CeO_2 > Pt/ZDC > Pt/LDC15>Pt/GDC10 > Pt/GDC30. All catalysts followed this trend but Pt/LDC15.
- Doping CeO_2 with La, Gd and Zr caused an ionic conductivity enhancement. A comparison of results showed the following trend: LDC15 > GDC10 > GDC30 > ZDC50 > CeO_2, where LDC15 showed the highest ionic conductivity.
- Pt-based catalysts were more stable than the Ni and Rh catalysts during the partial oxidation of methane.
- Pt/CeO_2 allowed higher and more stable CH_4 conversion than Pt/Al_2O_3, which may be due to the higher oxygen storage capacity of the former catalyst.
- Pt-based catalysts were fully regenerated after carbon build-up; initial conversions and selectivity were recovered.

Presentations

1. Salazar-Villalpando, Maria D.; Berry, David A.; Gardner, Todd H.; Shekhawat, Dushyant; Floyd, Donald. "Catalytic partial oxidation of methane on Rh-ceria based catalysts: Effect of reducibility", *accepted for presentation* at AIChE Fall Meeting, 2005.
2. Salazar-Villalpando, Maria D.; Berry, David A.; Gardner, Todd H.; Shekhawat, Dushyant. "Synthesis gas by partial oxidation and the role of oxygen-conducting supports: A review". Presented at the Second International Conference on Fuel Cell Science, Engineering and Technology, June 16, 2004.

FY 2005 Publications

1. Salazar-Villalpando, Maria D.; Berry, David A.; Gardner, Todd H.; Shekhawat, Dushyant; Celik, Ismail. Synthesis gas by partial oxidation and the role of oxygen-conducting supports: A review. Fuel Cell Science, Engineering and Technology, 2004, Rochester, New York, USA. Fuel Cell, 2004, p. 681-690.

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1. Applied Catalysis A: General 225(2002) 63-75.
2. Applied Catalysis B: Environmental 19 (1998) 267.
3. Catalysis by Ceria and Related Materials edited by A. Trovarelli. Catalytic Science Series. Vol. 2 Imperial College Press, 2002.